

THE MAGNETIC BEHAVIOR OF OZONE

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Professor G. N. Lewis suggested to the author that it would be interesting to measure the magnetic susceptibility of ozone. Becquerel¹ made such a measurement in 1881 and concluded that ozone was considerably more paramagnetic than oxygen. In the same year Schumeister,² while studying the magnetic behavior of oxygen, was led to a similar conclusion. Professor Lewis pointed out that this was a surprising result, since the ozone molecule is presumed to have no odd electrons.³

Becquerel's experiment, although only briefly described in his paper, was particularly simple and clear. A small hollow glass bar filled with air was suspended from its center horizontally by a gold wire, in a vessel between the poles of a magnet, the rest position of the bar making an angle of about 45° to the axis of the poles. In a magnetic field a couple will act upon the little bar, its magnitude depending on the strength and inhomogeneity of the field and on the difference between the susceptibility of the bar and of the surrounding medium. The angle through which the top of the wire had to be twisted to restore the bar to its original position in the presence of the field was measured in vacuum, in oxygen, and in two samples of ozonized oxygen. The torque in oxygen was much less than in vacuum, and in both ozone-oxygen mixtures it was still less, and was the least in the sample of higher concentration. Oxygen is paramagnetic and, therefore, from these data it appears that ozone is still more so. Quantitatively, assuming with Becquerel a value of ten volume per cent for his most concentrated sample, one finds the volume susceptibility of ozone to be more than three times that of oxygen.

So far as the author is aware no further work has been done on the magnetic properties of ozone. The experiment of Becquerel is described above in some detail, because its results differ radically from those obtained in the present experiment.

In the present work the Gouy method⁴ in its simple form was used. A cylindrical armature 20 cm. long and 8 mm. diameter, depending from one side of an analytical balance, hung vertically so that its lower end rested in the homogeneous field between the pole faces of the large electromagnet of this laboratory. The upper end was then practically out of the field. The force exercised by the field on the armature was measured with the balance when the armature was surrounded by air, by oxygen, and by an ozone-oxygen mixture.

To secure these conditions the armature hung in a vertical glass cylinder

of 18 mm. diameter, open at the top through a short length of 5 mm. bore tube, through which the suspending fibre passed. Oxygen or the ozone-oxygen mixture entered at the bottom of the cylinder, passing upward and out freely at the top. Air from the room was drawn into the cylinder by aspirating slowly at a point in the glass tube line connecting the ozone generator with the glass cylinder in the magnet.

The ozone was prepared electrolytically, the concentrations used in this work being 6-7% by volume. Pure oxygen was obtained by simply decomposing the ozone in the ozone-oxygen mixture by the passage of the mixture over a spiral of resistance wire heated to redness. Thus the generator was a source of oxygen or of ozone, depending on whether the spiral was at red heat or at room temperature.

Two armatures were used, both of nearly the same dimensions, the first composed entirely of pyrex glass and the second being a shell of soda-lime glass filled with oxygen at atmospheric pressure. The former, which was used in the first experiments, was quite strongly diamagnetic, while the latter, used in the last experiments, proved to be slightly more paramagnetic than a similar volume of oxygen.

The first experiments showed a difference between oxygen and the ozone-oxygen mixture, this being, however, only very little more than the errors in measurement. The difference was such as to indicate that ozone was less paramagnetic than oxygen; that is, the force on the diamagnetic armature in the mixture was less than it was in pure oxygen. With stronger fields the difference increased, but small variations in the field produced fluctuations in the total force in either gas of the same order of magnitude as the difference, which was a few tenths of a milligram. There appeared, nevertheless, a tendency for the force to be less in the ozone mixture than in pure oxygen, and in the first three experiments at three different field intensities the difference was greater than the difference calculated for the gases assuming the susceptibility of ozone to be zero.

The volume susceptibility of oxygen was taken as expressed by the formula

$$\kappa = \frac{1.221 \times 10^{10}}{T^2}, \text{ and of air by } \kappa = \frac{0.256 \times 10^{10}}{T^2}$$

at 1 atmosphere pressure.⁵ Two values of the susceptibility of the armature were had from two sets of measurements of the force in oxygen and in air, the first set at a low field strength yielding a less accurate result than the second. The values were -0.62×10^{-6} and -0.69×10^{-6} . The latter one has been used in these calculations, but either might be used without affecting the conclusions.

In view of the smallness of the effect and the magnitude of the errors of measurement, two experiments were performed on different days in which

a series of observations were made in each experiment on both oxygen and the ozone mixture, with the purpose of gaining an idea of the magnitude of the effect relative to the experimental errors. The results of these are given in figure 1. A smooth curve, No. 1 of the theoretical shape, that is, one in which the force varies as the square of the field intensity, has been drawn through the oxygen points. Relative to this, two calculated curves have been placed in the figure, No. 3 being that which Becquerel's results would indicate for this ozone concentration which was practically the same in the two experiments, and No. 2 that which should result if the suscepti-

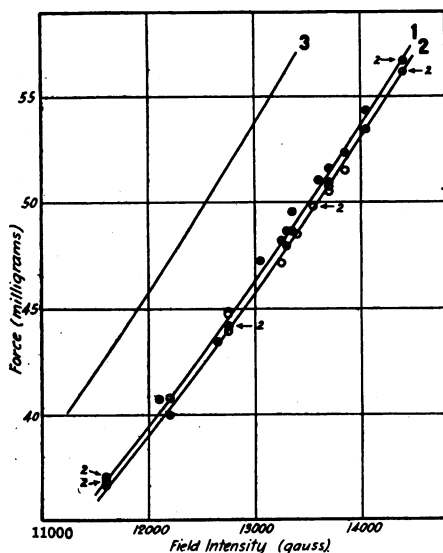


FIGURE 1

● Oxygen; ○ Ozone-Oxygen mixture.

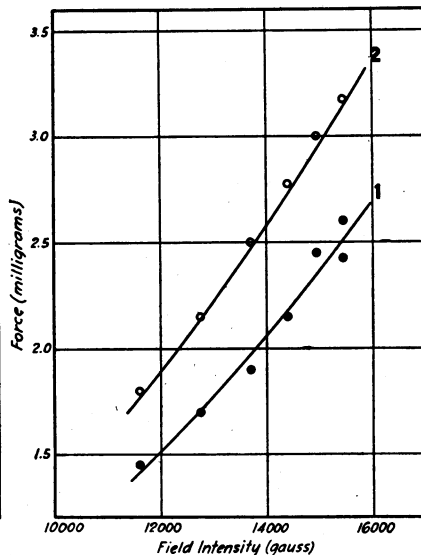


FIGURE 2

● Oxygen; ○ Ozone-Oxygen mixture.

bility of ozone were zero. In some cases observations fell at practically or identically the same point and are represented by a single point. These cases are indicated in the figure. Clearly the results are entirely different from those of Becquerel, and the points for ozone tend to lie below those for pure oxygen by an amount of the same order of magnitude as would be the case if the susceptibility of ozone were zero. It is also clear, however, that the results show fluctuations comparable with the effect itself. This is due chiefly to fluctuations in the field and to a lesser degree to the change in weight of the armature with changing room conditions and to direct errors of setting and reading.

To reduce the errors due to fluctuations in the field another armature was used, the second one described above, the attempt being made to have it of nearly the same susceptibility as oxygen. As mentioned, it was

slightly more paramagnetic than oxygen. The total force in oxygen was now small, and hence errors due to fluctuations in the field were correspondingly small. Three experiments on three different days, each consisting of a series of readings in oxygen and in an ozone-oxygen mixture, were performed with this armature, the technique of the measurements being successively improved. The results are shown in figures 2, 3 and 4. In each case a smooth curve, No. 1, of the theoretical shape, has been drawn through the oxygen points, and then a computed curve, No. 2, in which the susceptibility of ozone has been taken as zero, has been placed

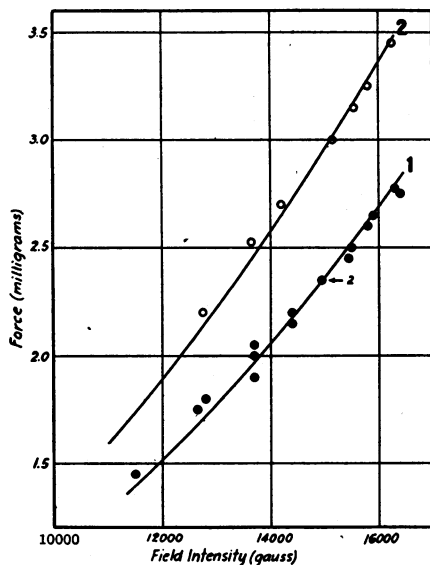


FIGURE 3

● Oxygen; ○ Ozone-Oxygen mixture.

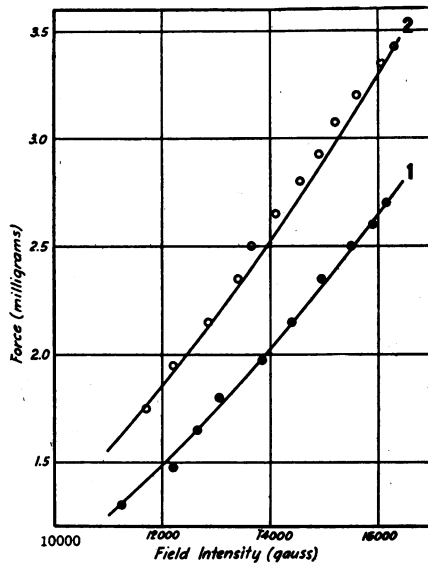


FIGURE 4

● Oxygen; ○ Ozone-Oxygen mixture.

upon the figure. In each case the curve required by Becquerel's results lies below the oxygen curve, and almost entirely off the figure.

Three sets of data for air and oxygen on these same days gave 0.174×10^{-6} , 0.174×10^{-6} and 0.173×10^{-6} for the volume susceptibility of the armature.

The results show that ozone is far from being more paramagnetic than oxygen. The tendency for the observations to lie above the computed curve in figures 2, 3 and 4 is evidence that ozone is diamagnetic, but the accuracy of these measurements does not permit a definite determination of the sign of the susceptibility. We can, however, conclude that the numerical value of the volume susceptibility of ozone is but a small fraction of that of oxygen. Thus the anomalous high paramagnetism of ozone recorded in the literature appears not to exist.

The author is glad to acknowledge his indebtedness to Professor G. N. Lewis for his interest and helpful suggestions; to Dr. Simon Freed for his kind advice throughout the work in a field with which the author was not familiar; and to Beatrice Wulf with whom much of the experimental work was done.

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¹ Becquerel, *Compt. rend.*, **92**, 348 (1881).

² Schumeister, *Sitz. Akad. Wiss. Wien*, II, **83**, 45 (1881).

³ Lewis, *Valence and the Structure of Atoms and Molecules*, Chemical Catalog Co., 1923, pages 130, 147 et seq; *Chemical Reviews*, **1**, 234 (1924).

⁴ See, for example, Stoner, *Magnetism and Atomic Structure*, E. P. Dutton and Co., 1926, page 40.

⁵ The expression for oxygen was calculated from an average value of the volume susceptibility using the three recent values listed by Stoner in Table IX of his book, see ref. 4. The expression for air was obtained from this and from the composition of air, taking account of the oxygen only.

GENERAL ARITHMETIC

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The abstract theory of a mathematical system consisting of a set of elements and two operations "multiplication," and, later, "addition" is developed by postulational methods with examples.

The more important results are the following. An "arithmetic" may be roughly described as a system in which

1. Every element is completely specified by a finite number of cardinal numbers.

2. "Division" is not always possible, and we can find when one element divides another element in a finite number of steps.

3. Unique resolution into "prime factors" is always possible.

For the case when multiplication is commutative we replace these vague requirements by an exact set of postulates, the necessary and sufficient conditions for a system to form an arithmetic. We give a general theory of recurring sequences, exhibiting the connections with the Dedekind field theory which we develop following Kronecker, as an arithmetic of forms without assuming the so-called "fundamental theorem of algebra." We next show that all systems of ideals and ideal numbers are abstractly equivalent and may be replaced by the system of rational integers, making ideals and ideal numbers unnecessary in algebraic arithmetic.

An arithmetic may be defined over any arbitrary class of distinct de-